

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification 6 : C09K 3/14, C09D 9/02 // D21H 19/20</p>	<p>A1</p>	<p>(11) International Publication Number: WO 97/20009 (43) International Publication Date: 5 June 1997 (05.06.97)</p>
<p>(21) International Application Number: PCT/KR96/00217 (22) International Filing Date: 27 November 1996 (27.11.96) (30) Priority Data: 1995/43894 27 November 1995 (27.11.95) KR (71) Applicant (for all designated States except US): KOREA RE-SEARCH INSTITUTE OF CHEMICAL TECHNOLOGY [KR/KR]; 100, Jang-dong, Yusung-ku, Daejeon 305-343 (KR). (72) Inventors; and (75) Inventors/Applicants (for US only): PARK, In-Hwan [KR/KR]; Hyundai Apartment 101-102, 431-6, Doryong-dong, Yusung-ku, Daejeon 305-340 (KR). JANG, Ja-Soon [KR/KR]; Lotte Apartment 120-601, 220, Nae-dong, Seo-ku, Daejeon 302-181 (KR). SEOL, Sang-Won [KR/KR]; Mokdongsinsigaji Apartment 1215-1505, 326, Sinjung-dong, Yangcheon-ku, Seoul 158-070 (KR). SUH, Jung-Mok [KR/KR]; Woosung Apartment 127-102, 640, Junggrim-dong, Seo-ku, Daejeon 302-230 (KR). (74) Agent: HUH, Sang, Hoon; Hyecheon Building, 13th floor, 831, Yeoksam-dong, Kangnam-ku, Seoul 135-792 (KR).</p>		<p>(81) Designated States: CN, JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  Published With international search report.</p>
<p>(54) Title: PROCESS FOR MANUFACTURING AN ACRYLIC ANTISLIPPING AGENT COMPOSED OF SMALL AMOUNTS OF SOLID CONTENT</p>		
<p>(57) Abstract  This invention relates to a process for manufacturing a highly efficient antislipping agent composed of acrylic copolymers based on a small amount of solid content; wherein two kinds of acrylic latexes composed each of small amounts of solid content are prepared by using pertinent acrylic monomers in each side of low or high glass transition points, followed by neutralizing with ammonia water. Thus, the latices are well blended and their physical properties such as tacky property, flexibility, hardness and viscosity can be easily controlled.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

## PROCESS FOR MANUFACTURING AN ACRYLIC ANTISLIPPING AGENT COMPOSED OF SMALL AMOUNTS OF SOLID CONTENT

### BACKGROUND OF THE INVENTION

#### 5 Field of the Invention

This invention relates to a process for manufacturing a highly efficient antislipping agent composed of acrylic copolymers based on small amounts of solid content; wherein two kinds of acrylic latexes composed of small amounts of solid content are prepared by using pertinent acrylic monomers in low or  
10 high glass transition point side, being well blended and homogenized by neutralizing with ammonia water.

#### Description of the Related Art

According to the composition of antislipping agents in the first stage, some hot-melt adhesives were coated along several lines on the surfaces of  
15 packaging boxes made of craft paper, the adhesives proved to have antislipping effects owing to its initial strong adhesive strength when stacking packaging boxes and some disadvantages were recognized in that a) separation between packaging boxes were difficult, and b) after separation, the packaging surfaces are torn or stained, thus inflicting some damages to the  
20 surfaces due to extremely strong adhesive strength [Japanese Patent Unexamined Publication No. 1-183596(1989)].

To be free from weak points, some antislipping agents as a hybrid of inorganic and organic substances were developed:

a) Inorganic substance included silicahydrosol containing 20 to 30 wt% of  
25 colloidal silica whose particle size was in the range of 10 to 20  $\mu\text{m}$ . Silicahydrosol in liquid phase was useful not to be whitened in handling when coated or dried. Now that said the size was too small, however, its homogeneous dispersion was so difficult that desirable antislipping effects

could not be gained [Canadian Patent No. 1,156,803(1980), Japanese Patent Unexamined Publication Nos. 2-245086 (1990) and 4-303653 (1992)].

- b) Organic substance composed of styrene and acrylic acid as well as some composition with reactive groups proved to have less antislipping effects  
5 [Japanese Patent Unexamined Publication No. 57-565989 (1982)].

Further, some antislipping agents containing inorganic and organic substances concurrently included a composition in which synthetic resin binder, using silica powder and poly(acrylamide) treated with nonionic cellulose derivatives as a protective colloid, was dispersed in water. After  
10 the agents were coated or dried, they showed good antislipping effects but when used repeatedly, its antislipping effects become deteriorated and in particular, a poor dispersion of antislipping agent itself affected its storage stability badly [Japanese Patent Unexamined Publication No. 59-4460 (1984)].

In view of facts above-mentioned, there were some methods in which a  
15 part of resin with adhesive strength was blended to ethylene-vinyl acetate copolymer emulsion, followed by additional blending of silica, fillers and releasing agents. However, the methods proved to have insufficient antislipping effects and when packaging boxes were separated, their surfaces were torn off or contaminated owing to its extremely strong adhesive strength  
20 or the lack of reutilization [Japanese Patent Unexamined Publication No. 54-65385(1988), 62-70461(1987), 62-110997(1987) and 4-198373(1992)].

Recently, some latex-typed antislipping agents using nonionic surfactants as a emulsifier were developed. Each particle in the latex consists of both a core as a hard segment and a shell as a soft segment and when  
25 drying, it showed good antislipping properties. But since there was no distinction between hard and soft segments with increasing of solid content in the latex, it was still difficult to prepare a latex with storage stability [Japanese Patent Unexamined Publication No. 4-306273(1992)].

## SUMMARY OF THE INVENTION

The object of this invention is to provide a process for manufacturing an antislipping agent with high viscosity, latex-typed compounds with storage stability, being characterized by the facts that an antislipping agent with small amounts of solid content mentioned in the above has a good harmony between hard and soft segments as well as its storage stability.

This invention is to provide a process for manufacturing an antislipping agent characterized by comprising steps of;

- 1) through the emulsion polymerization between acrylic monomers of 20 to 80 wt% with glass transition point(Tg) in the range of -85 to -5 °C and acrylic monomers of 20 to 80 wt% with Tg in the range of 8 to 153 °C, an acrylic latex with relatively low scope of Tg is prepared;
- 2) through another emulsion polymerization in another container between acrylic monomers of 10 to 60 wt% with Tg in the range of 8 to 153 °C and acrylic monomers of 40 to 90 wt% with Tg in the range of -85 to -5 °C an acrylic latex with relatively high scope of Tg is prepared; and
- 3) the acrylic latex mentioned in the step 2) of 5 to 60 wt parts is chemically blended with that in the step 1) of 100 wt parts, and the blending is completed by neutralizing with ammonia water.

## DETAILED DESCRIPTION OF THE INVENTION

This invention relates to a process for manufacturing an antislipping agent composed of small amounts of solid content, wherein an acrylic latex having low Tg is blended in a certain ratio with an acrylic latex having high Tg and after neutralization, and if necessary, an inorganic compound and its blending/dispersing agents may be added to the blend.

More detailed process for manufacturing an acrylic antislipping agents of this invention is as follows:

In an effort to prepare an acrylic latex with flexibility according to this invention, acrylic monomers(viscosity : 10 to 30 cps) having low Tg in the range of -85 to -5 °C are selected and these monomers provide adhesive strength to an antislipping agent of this invention.

5 More specifically, the monomers include ethylacrylate, n-butylacrylate, isopropylacrylate, 2-ethylhexylacrylate, n-hexylmetacrylate, laurylmetacrylate, 2-hydroxyethylacrylate and hydroxypropylacrylate, and one or more acrylic monomers may be used. In case of preparing an acrylic latex having low Tg in the range of -85 to -5 °C, the content of monomers should be preferably in  
10 the range of 20 to 80 wt%. Should the content be less than 20 wt%, an antislipping agent itself, prepared through emulsion polymerization, lacks the antislipping effects due to the hardness and insufficient tacky property but if the content exceed 80 wt%, its insufficient, cohesive force due to the excessive flexibility may lead to decreasing the antislipping effects, while having high  
15 tacky property when dried.

Further, in order to prepare an acrylic latex with good storage stability, an aqueous cellulose is used to enhance the viscosity of an dispersed solution. More specifically, the celluloses mentioned here include methycellulose, ethylcellulose, hydroxyethylcellulose and hydroxypropylmethylcellulose.  
20 Hence, one or more celluloses may be used with 0.05 to 20 wt parts in proportion to 100 wt parts of water, a polymerization solvent.

In general, when small amounts of monomers are under emulsion polymerization, far less content of celluloses designed for the dispersion may be responsible for a latex without dispersion stability.

25 However, in the event that celluloses are employed to reaction solvents in the range of scope above-mentioned, the viscosity in reaction solution increased and acrylic monomers dropped as a liquid phase are favorably dispersed, showing the polymerization with dispersion stability. An acrylic

latex, so formed, is favorable in terms of its storage stability and despite less solid content of the latex, the antislipping effects prove to be desirable. Hence, if the content of celluloses for dispersion is less than 0.05 wt parts, there are little dispersion effects associated with the viscosity of reaction solvent and the emulsion polymerization is not well progressed. Nevertheless, if the content of celluloses for dispersion exceeds 20 wt parts, the disperse force is on the contrary decreased due to high viscosity of the reaction solution in emulsion polymerization.

In order to provide the hardness to an antislipping agent of this invention, another acrylic latex having relatively high Tg in the range of 8 to 153 °C is prepared by emulsion polymerization and then blended with the acrylic latex, so obtained in the above.

More specifically, the monomers include methylacrylate, methylmetacrylate, ethylmetacrylate, isobutylmetacrylate, 2-hydroxymethylmetacrylate, hydroxypropylmetacrylate, acrylamide, diacetoneacrylamide, glycidylmetacrylate, styrene, vinylacetate and acrylonitrile, etc. Among them one or more monomers can be employed.

In line with the preparation of an acrylic latex having high Tg, acrylic monomers of 10 to 60 wt% having Tg in the range of 8 to 153 °C should be preferably contained. If the content is less than 10 wt%, the cohesive force of an antislipping agent itself become weak and in case of exceeding 60 wt%, the antislipping effects don't exist due to the lack of tacky property.

The emulsion polymerization of this invention is stirred at 100 to 300 rpm under nitrogen atmosphere at 50 to 80 °C and radical initiators for the polymerization are employed. More specifically, the initiators include ammonium persulfate, potassium persulfate, 4, 4'-azobis-4-cyanopentanoic acid, azobisisobutyramidine, potassium peroxide, hydrogen peroxide and cumenhydroperoxide. The appropriate amount of initiators is 0.02 to 5 wt

parts in proportion to a total monomer of 100 wt parts. If the amount of initiators is less than scope in the above, the polymerization speed is quite fast or slow and in case of outside of the scope, an latex with dispersion stability is not obtained.

5 Further, crosslinking agents include divinylbenzene, butylmelamine, di- or tri-urethane acrylate, trimethylolpropane trimetacrylate and N, N'-methylenebisacrylamide. The amount of the crosslinking agents is in the range of  $0.2 \times 10^{-3}$  to  $5 \times 10^{-3}$  wt parts in proportion to a total monomer of 100 wt parts. If the amount of crosslinking agents is less or more than scope in  
10 the above, the tacky property of an antislipping agent comes to decrease.

Also, in order to the additional adhesive strength to an antislipping agent, some monomers, having various kinds of carboxylic acids, are employed in the emulsion polymerization as above-mentioned. One or more monomers selected from acrylic acid, metacrylic acid, maleic acid and itaconic  
15 acid are used. The amount of the monomers used in emulsion polymerization is in the range of 0.05 to 7 wt parts in proportion to a total monomer of 100 wt parts. Hence, if the content of these monomers is less than 0.05 wt parts, the antislipping effects are not noticeable due to the lack of adhesive strength and in case of exceeding 7 wt parts, the emulsion  
20 polymerization becomes unstable under acidic media caused by lumping of latexes.

According to this invention, anionic and nonionic surfactants may be used individually or concurrently for the emulsion polymerization, where the stability of a latex is greatly affected by the kinds and amounts of surfactants.

25 The anionic surfactant includes sodium alkylbenzene sulfonate, sodium alkylsulfate, sodium alkylsulfonate, sodium dialkylsulfosuccinate, fatty acid soap, sodium alkylethoxysulfate, alkylphenoethoxylate and fatty acid ethoxylate.



The nonionic surfactants include one having HLB (Hydrophilic Lipophilic Balance) value of 8 to 18; for example, polyethyleneglycol nonylphenylether, polyethyleneglycol octylphenylether, polyethyleneglycol dodecylphenylether, polyethyleneglycol alkylarylether, polyethyleneglycol  
5 oleyl ether, polyethyleneglycol laurylether, polyethyleneglycol alkylphenyl ether, polyethyleneglycol olefinic acid ether, polyethyleneglycol distearic acid ether, polyethyleneglycol sorbitan monolaurate, polyethyleneglycol sorbitan monostearte, polyethyleneglycol alkylether, polyoxiethylenelauryl alcohol ether, and polyoxiethylenelauryl fatty acid ester. They are used one or a  
10 mixture of two. The appropriate amount of the surfactants is in the range of  $0.2 \times 10^{-4}$  to  $1 \times 10^{-2}$  wt parts in proportion to 100 wt parts of water, a reaction solvent. Hence, if the amount is less than  $0.2 \times 10^{-4}$  wt parts, the latex is liable to be broken easily and in case of exceeding  $1 \times 10^{-2}$  wt parts, the interfacial tension of an antislipping agent is on the contrary decreased.

15 In order to modulate the molecular weight of a latex in this invention, chain transition agents are used. More specifically, the agents include carbon tetrachloride, carbon tetrabromide, dodecylmercaptan and n-butylmercaptan. The amount is 0.005 to 5 wt parts in proportion to a total monomer of 100 wt parts. If this amount is less than scope in the above, their effects are not  
20 noticeable and in case of exceeding scope in the above, the polymerization speed is quite slow and a resin with flexibility cannot be produced due to its smaller molecular weights.

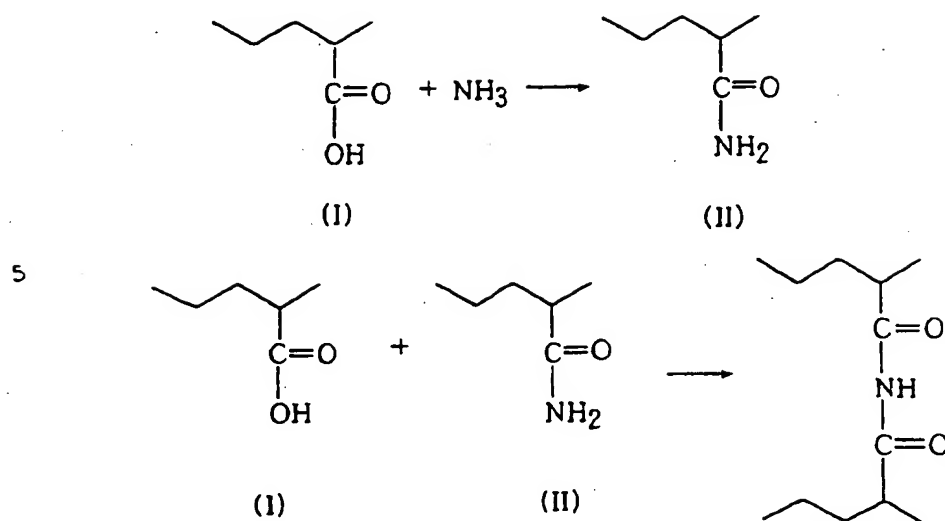
In order to blend an acrylic latex having low Tg and another acrylic latex having high Tg in the range of pH 2 to 5, ammonia water in 10%  
25 concentration is used. The appropriate scope of pH during neutralization is 6 to 8 and at any pH excluding the scope, the storage stability of the blended latex is significantly decreased. Hence, as for the blending ratio, an acrylic latex having high Tg of 5 to 60 wt parts is blended in proportion to an acrylic

latex having low Tg of 100 wt parts, and then if the blending ratio is less than 5 wt parts, the viscosity of the latex is low and in case of exceeding 60 wt parts, the antislipping effects are decreased due to higher hardness.

Further, in order to allow more antislipping effects to an latex prepared  
5 in said blending in this invention, inorganic compounds (e.g., silica powder, silica gel, glass powder, talc, clay, calcium carbonate, magnesium carbonate, zinc oxide, barium sulfate, etc.) are added, however, in case of using silica and/or glass powder, the surface is previously coated by silane coupling  
agents (e.g.,  $\gamma$ -aminopropyltriethoxysilane,  $\gamma$   
10 -glydoxypropyltrimethoxysilane, etc.) and followed by thermal reaction at 80 to 100°C for 0.5 to 2 hours prior to use the powders. The amount of inorganic compounds is 0.03 to 12 wt parts in proportion to 100 wt parts of an latex prepared by blending as the condition in the above. If the content of inorganic compounds is less than 0.03 wt parts, any antislipping effects are not  
15 noticeable, and in case of exceeding 12 wt parts, the adhesive strength becomes poor due to a larger cohesive force.

During the storage of these antislipping agents, their stability can be gained by chemically binding between two kinds of acrylic latexes with carboxylic acid groups and ammonia water. Further, when antislipping  
20 agents in the above are coated and dried, the cross-linking reaction with imide bond partially occurs between carboxylic acid groups in the latex and ammonia as the following reaction scheme [German Patent No. 868,130 in 1858)]. Cross-linking reactions like this among latexes may bring forth some benefits such as the good homogenization as well as the increase of the  
25 mechanical strength.

9



In the meanwhile, in order to blend some latexes obtained in the above and an inorganic compound like silica together one or more of various types of dispersing agents in this invention (e.g., casein, gelatin, polymer organic acid ammonium salt, acrylic polymer aqueous solution, sodium polyacrylate, denatured sodium polyacrylate, etc.) are used. The amount of the inorganic compounds is 0.05 to 5 wt parts in proportion to 100 wt parts of the antislipping agent. If the amount is less than 0.05 wt parts, the dispersing agent is less effective, and in case of exceeding 5 wt parts, the cohesive force of an antislipping agent itself is decreased.

In line with an antislipping agent, so prepared by a process of the invention mentioned in the above, the solid content is adjusted in the range of 2 to 8 wt%, being relatively less than that of 30 to 50 wt% of ordinary antislipping agents, and the viscosity of an antislipping agent in this invention is in the scope of 100 to 2,000 cps. Therefore, the effects of this invention are that a) since an antislipping agent has an appropriate viscosity, in case of coating on a packaging box made of craft paper by spray method, the working procedure is convenient, and b) since latexes on a packaging box are well dispersed in order to have appropriate hardness and flexibility, coated and

dried, the antislipping effect may be noticeable.

This invention will be explained in more detail by the following examples, but the claims are not limited to these examples.

#### EXAMPLES 1 to 18

5       Based upon the composition as illustrated in the following Table 1, 0.8 g of polyethyleneglycol nonylphenylether (10 wt%), 1.17 g of sodium alkylbenzene sulfonate (10 wt%), 0.17 g of ammonium persulphate,  $1.64 \times 10^{-3}$  g of divinylbenzene and 0.10 g of acrylic acid were charged to 100 g of hydroxyethylcellulose solution (0.5 wt parts) in a round flask (250 cc) equipped with a dropping funnel and stirred for about 30 minutes. Meantime,  
10       a mixture of 1.17 g of methylmetacrylate, 1.17 g of butylacrylate, 1.67 g of ethylacrylate and 0.08 g of carbon tetrabromide was charged to another flask (50 cc). This mixture was dropwisely added to the above flask, and stirred and emulsified. While the emulsified solution were dropped at the speed of  
15       1 to 2 drops-per second through a dropping funnel in a reactor (reaction temperature: 70 °C, stirring rate : 120 rpm) equipped with a reflux condenser under inert atmosphere, the reaction was performed for 4 to 5 hours.

      The reactant was cooled to room temperature and neutralized at pH 7 though the addition of 10 wt% of ammonia water (12.21 g). Thereafter, as  
20       2.20g of another latex adjusted Tg at 37.2 °C was added to neutralized latex together with 0.50 g of silicasol coupled with 0.05g of  $\gamma$ -aminopropyltriethoxysilane, and then was blended at 120 rpm for 20 to 30 minutes to obtain the good dispersion.

#### COMPARATIVE EXAMPLES 1 to 17

25       Based upon the composition as illustrated in the following Table 1, 0.8 g of polyethyleneglycol nonylphenylether (10 wt%), 1.17 g of sodium alkylbenzene sulfonate (10 wt%), 0.17 g of ammonium persulphate and 0.05 g of acrylic acid were charged to 100 g of distilled water in a round flask of the

same type as mentioned in the above Examples 1 to 18. Meantime, a mixture of 1.17 g of methylmetacrylate, 1.17 g of butylacrylate, 1.67 g of ethylacrylate and 0.08 g of carbon tetrabromide was charged to another flask (50 cc). This mixture was dropwisely added in the above flask, and stirred to be emulsified.

5 While the emulsified solution, through a dropping tunnel, were dropped at the speed of 1 to 2 drops per second in a reactor (reaction temperature: 70°C, stirring rate : 120 rpm) equipped with a reflux condenser under inert atmosphere, the reaction was performed for 4 to 5 hours. As the result, an inhomogeneous products from emulsion polymerization were gained. This  
10 was attributed to the fact that since the content of thickeners, playing as a dispersing stabilizer in the reaction solution for dispersion, were small and thus, a part of disordinary products with inhomogeneity is gained.

On the other hand, in case of comparative examples 2 and 3, 0.65 to 0.80 wt parts of hydroxyethylcellulose were added into distilled water to obtain  
15 homogeneous products in emulsion polymerization. However, due to less use of thickeners, the adhesive force and the reusability were proved to be poor. Meantime, to stabilize the latex solutions, they were neutralized based upon the same manner as mentioned in the above Examples 1 to 18. As shown in Comparative examples 13 and 14 on Table 1, in the event that the reaction was  
20 not stabilized by adding relatively larger amounts of acrylic acid in monomer composition, latexes were broken and produced a part of lumps together and thus, physical properties were remarkably decreased. Further, as mentioned in comparative example 1, in the event that the reaction were performed by adding relatively larger amounts of methylmetacrylate in  
25 monomer composition, the products when dried, so formed, were extremely hard and thus, the antislipping effects were proved to be poor. As illustrated in comparative example 8, in the event that the reaction was performed by adding relatively larger amounts of hydroxyethylcellulose in monomer

composition, monomers were not dispersed well and inhomogeneous products were obtained due to the increase of the viscosity.

5

10

15

---

20

25

Table 1.

Examples	Composition of monomers <sup>a</sup> (wt parts)						Additives(wt parts)		Antislipping agents	Solids conc. (wt%)			
	MMA	BA	EA	AA	MA	DVB ( $\times 10^3$ )	HEC	Latex <sup>b</sup>			Silicasol <sup>c</sup>		
1	7.02	1.88	7.14	0.40	-	8.58	1.50	3.00	2.00	31.7	O/ $\Delta$ /O/ $\times$	35	22.9
2	4.98	2.32	7.12	0.36	-	5.91	1.20	2.75	1.60	18.9	O/ $\Delta$ /O/ $\times$	37	20.3
3	3.61	2.36	5.57	0.29	-	4.73	1.00	2.50	1.00	13.5	O/ $\Delta$ /O/ $\times$	39	16.3
4	2.45	1.81	4.04	0.20	-	3.40	0.90	2.30	0.80	10.8	O/ $\Delta$ /O/ $\Delta$	38	12.5
5	1.88	1.40	3.38	0.16	-	2.72	0.70	2.25	0.70	9.2	O/O/O/ $\Delta$	42	10.5
6	1.17	1.17	1.87	0.10	-	1.84	0.50	2.10	0.50	8.2	O/O/O/O	44	7.2
7	1.17	1.17	1.87	-	0.10	1.84	0.50	2.10	0.50	8.7	O/O/O/O	43	7.2
8	1.05	1.50	1.05	-	0.09	1.48	0.50	2.00	0.40	4.8	O/O/ $\Delta$ / $\Delta$	47	6.6
9	0.52	1.12	1.16	0.08	-	1.14	0.40	1.10	0.20	-8.8	O/O/ $\Delta$ / $\times$	49	4.6
10	0.35	1.12	1.33	0.08	-	1.14	0.40	1.10	0.20	-18.3	O/O/ $\times$ / $\times$	51	4.6
11	0.27	1.37	1.16	0.08	-	1.14	0.40	1.10	0.20	-22.7	O/O/ $\times$ / $\times$	53	4.6
12	0.82	1.16	0.82	0.08	-	1.14	0.40	1.10	0.20	41	O/ $\Delta$ /O/ $\Delta$	37	4.6
13	0.82	1.16	0.82	0.08	-	1.14	0.30	1.10	0.10	4.1	$\Delta$ / $\Delta$ /O/ $\Delta$	38	4.4
14	0.58	0.58	0.84	0.04	-	0.82	0.40	0.90	0.20	7.5	O/ $\Delta$ /O/ $\Delta$	37	3.5
15	0.58	0.84	0.58	-	0.04	0.82	0.40	0.90	0.10	3.9	O/ $\Delta$ / $\Delta$ / $\Delta$	39	3.4
16	0.35	0.35	0.50	0.03	-	0.49	0.40	1.10	0.10	8.2	O/ $\Delta$ /O/ $\Delta$	36	2.8
17	0.35	0.50	0.35	-	0.03	0.49	0.40	1.10	-	4.8	O/ $\Delta$ / $\Delta$ / $\Delta$	37	2.7
18	0.25	0.45	0.55	0.03	-	0.51	0.30	-	-	-5.4	O/ $\Delta$ /O/ $\Delta$	40	2.7

To be continued

Comp. Examples	Composition of monomers <sup>a</sup> (wt parts)						Additives(wt parts)			Antislipping agents			
	MMA	BA	EA	AA	MA	DVB (x10 <sup>3</sup> )	HEC	Latex <sup>b</sup>	Silicasol <sup>c</sup>	Polymer Tg <sup>d</sup> (°C)	Homogeneity/Adhesiveness /Hardness/Reusability <sup>e</sup>	Slipping angle <sup>f</sup> (°)	Solids conc. (wt%)
1	3.61	2.36	5.57	0.29	-	4.73	1.00	-	-	13.5	O/x/O/x	-	12.8
2	1.87	1.87	2.67	0.16	-	2.82	0.80	1.10	-	8.2	O/Δ/O/Δ	33	8.5
3	1.52	1.52	2.17	0.13	-	2.14	0.85	0.90	-	8.2	O/Δ/O/Δ	32	8.9
4	1.17	1.17	1.87	-	0.10	1.84	-	0.08	-	8.7	x/x/x/x	-	5.0
5	1.17	1.17	1.87	0.05	-	-	0.10	-	-	7.0	Δ/x/Δ/x	-	4.2
6	1.17	1.17	1.87	0.05	-	-	0.20	-	-	7.0	x/x/O/x	-	4.3
7	1.17	1.17	1.87	0.05	-	-	0.50	-	-	7.0	O/x/O/Δ	-	4.6
8	1.17	1.17	1.87	0.03	-	-	1.20	-	-	6.7	Δ/x/Δ/Δ	-	5.2
9	0.92	1.44	1.87	0.10	-	-	0.50	-	0.50	-1.8	O/Δ/Δ/Δ	27	5.1
10	0.92	1.44	1.87	0.07	-	-	0.40	-	0.20	-2.8	O/x/Δ/Δ	25	4.7
11	0.92	1.67	1.44	0.07	-	-	0.40	-	-	-4.4	O/x/Δ/Δ	-	4.5
12	0.45	1.17	1.16	-	0.06	1.14	0.40	-	-	-11.0	O/x/x/x	-	3.2
13	0.82	0.82	1.16	-	0.30	1.24	0.40	-	-	8.0	x/x/Δ/x	-	3.5
14	0.58	0.58	0.84	-	0.20	-	0.40	-	-	16.9	x/x/Δ/x	-	2.6
15	0.58	0.58	0.84	0.04	-	-	0.30	-	-	7.5	O/x/O/x	-	2.3
16	0.35	0.50	0.35	-	0.06	-	0.20	0.90	-	5.9	Δ/Δ/O/Δ	30	2.4
17	0.35	0.50	0.35	-	-	-	0.07	-	-	1.7	x/x/x/x	-	1.3



## [Note]

- a: MMA - methylmetacrylate, BA - butylacrylate, EA - ethylacrylate, AA - acrylic acid, MA - metacrylic acid, DVB - divinylbenzene, HEC - hydroxyethylcellulose. All figures are the weight of each substance per 100 g of distilled water.
- b: A latex of 10 wt% at relatively high  $T_g(=37.2^{\circ}\text{C})$ , manufactured by styrene, butylacrylate and metacrylic acid.
- c: Silicasol of 30 wt parts.
- d: Theoretical value based upon only the composition of monomers.
- e: Reutilization ability examined from surface damage and contamination caused by strong adhesion ( $\bigcirc$  : high,  $\triangle$  : middle,  $\times$  : low).
- f: An antislipping agent was sprayed and after hardening for 30 minutes, this value was decided from the friction coefficient measured by a slant method for paper and pasteboard of JIS P 8147.
- A pendulum prepared by stainless steel (width: 60 mm, length: 100 mm, weight: 1,000 g).
- The slant speed of a slant plate was less than  $3^{\circ}$  per second.
- The slant angle was measured when a packaging box raised on a slant plate was slipped with the increase of the slant angle.

According to said Table 1, it was revealed as followings:

In Examples of this invention, aqueous hydroxyethylcellulose was used for increasing the viscosity of solution and then, the emulsion polymerization reaction was performed mainly with acryl monomers having low  $T_g$  to give a latex with dispersion stability. As the result, said compound itself has the antislipping effects. However, in order to prepare an antislipping agent with the more remarkable antislipping effects, in this invention, another acrylic monomer having relatively high  $T_g$  was blended with previously prepared latex, and some additives such as silica were added to the mixture. Now that

the blending material exhibits a remarkable antislipping effect and it is available for a stable storage and transportation after stacked on any packaging box made of craft paper.

5

10

15

20

25

## WHAT IS CLAIMED IS :

1. A process for manufacturing an acrylic antislipping agent, characterized by comprising steps of
  - 5 1) through the emulsion polymerization between acrylic monomer of 20 to 80 wt% with glass transition temperature (Tg) in the range of -85 to -5 °C and acrylic monomers of 20 to 80 wt% with Tg in the range of 8 to 153 °C, an acrylic latex with relatively low scope of Tg is prepared;
  - 10 2) through another emulsion polymerization in another container between acrylic monomer of 10 to 60 wt% with Tg in the range of 8 to 153 °C and acrylic monomer of 40 to 90 wt% with Tg in the range of -85 to -5 °C, an acrylic latex with relatively high scope of Tg is prepared; and
  - 15 3) the acrylic latex mentioned in the step 2) of 5 to 60 wt parts is chemically blended with that in the step 1) of 100 wt parts, and the blending is completed by neutralizing with ammonia water.
2. The process for manufacturing an acrylic antislipping agent according
  - 20 to claim 1, wherein in processes of said step 1) and 2), monomers with carboxylic acid groups are used within 0.05 to 7 wt parts for the total amount of the monomers used in the preparation of an antislipping agent.
- 25 3. The process for manufacturing an acrylic antislipping agent according to claim 2, wherein one or more monomers with carboxylic acid group selected from acrylic acid, metacrylic acid and maleic acid and itaconic acid are used.

4. The process for manufacturing an acrylic antislipping agent according to claim 1, wherein in step 1) above-mentioned, one or more monomers selected from ethylacrylate, n-butylacrylate, isopropylacrylate, 2-ethylhexylacrylate, n-hexylmetacrylate, laurylmetacrylate, 2-hydroxyethylacrylate and hydroxypropylacrylate are used.
5. The process for manufacturing an acrylic antislipping agent according to claim 1, wherein in step 2) above mentioned, one or more monomers selected from methyl acrylate, methylmetacrylate, ethylmetacrylate, isobutylmetacrylate, 2-hydroxyethylmetacrylate, hydroxypropylmetacrylate, acrylamide, diacetone acrylamide, glycidylmetacrylate, styrene, vinylacetate and acrylonitrile are used.
6. The process for manufacturing an acrylic antislipping agent according to claim 1, wherein the solid content in a final acylic latex obtained from step 3) are adjusted to 2 to 8 wt% for the total amount of the solid content used in the preparation of the latex.

# INTERNATIONAL SEARCH REPORT

International application No. II

PCT/KR 96/00217

## A. CLASSIFICATION OF SUBJECT MATTER

IPC<sup>6</sup>: C 09 K 3/14; C 09 D 9/02 // D 21 H 19/20

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC<sup>6</sup>: C 09 K; D 21 H; C 09 D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPIL

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Patent Abstracts of Japan, Vol.14, No.188 (C-710), 1990, JP 2-34671 A (MITSUI TOATSU CHEM. INC.).	1-6
A	Derwent Accession No.92-404515, Questel Telesystems (WPIL), Derwent Publications Ltd., London, abstracts; & JP 04-303653 A (TOPPAN PRINTING CO., LTD.).	1-6
A	Patent Abstracts of Japan, Japanese Patent Office, No. 6-80953 A 22 March 1994 (22.03.94).	1-6
A	EP 0 350 834 A2 (DIC HERCULES CHEMICALS, INC.) 17 January 1990 (17.01.90), page 2, line 51 - page 3, line 13; examples; claims.	1-6

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

\* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

20 February 1997 (20.02.97)

Date of mailing of the international search report

06 March 1997 (06.03.97)

Name and mailing address of the ISA/AT  
AUSTRIAN PATENT OFFICE  
Kohlmarkt 8-10  
A-1014 Vienna  
Facsimile No. 1/53424/535

Authorized officer

Tengler

Telephone No. 1/53424/213

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.

PCT/KR 96/00217

le Recherchebericht angeführt Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
EP A2 350834	17-01-90	DE C0 68918645	10-11-94
		DE T2 68918645	30-03-95
		EP A5 350834	05-06-91
		EP B1 350834	05-10-94
		JP A2 2026997	29-01-90
		US A 5079303	07-01-92